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s_1/s_2, X_{12}, and Q_{12} parameter values proposed in the literature.

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Communications to the Editor

Influence of Stretched and Unstretched Low-Density Polyethylene on the Photochemistry of a Conformationally Labile Ketone Dopant[1]

A wide variety of order solvents have been employed to alter the thermal and photochemical reactivities of solutes.[2] Alternatively, careful analyses of phase-dependent changes in reaction selectivities can be used to characterize the microenvironments of solutes. In principle, the simpler the solvent system, the greater will be the potential for obtaining useful structural and dynamic information from solute reactions.

Long *n*-alkanes are recognized to be "simple" isotropic liquids which contain small domains of longitudinal alignment.[3] The fluxional behavior of these liquids and the weakness of the van der Waals forces responsible for their alignment have made the domains of little practical use.[4] We view low-density polyethylene (LDPE) as an extremely viscous hydrocarbon solvent in which alkyl chains experience extensive local, semipermanent ordering[5] much like that of nematic liquid-crystalline phases.[6] As such, it may allow the effect of solvent chain alignment on solute reactivity to be observed in ways which are unavailable to *n*-alkanes.

In spite of its potential, very few examples of LDPE as a reaction medium have appeared. The photodimerization of tetraphenylbutatriene[7a] and the Norrish II reactions of 2-alkanones[7b] are the only examples of which we are aware. The first reaction is the sole example in which a comparison between reactivity in stretched and unstretched LDPE has been made. A threefold increase in quantum

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Scheme I

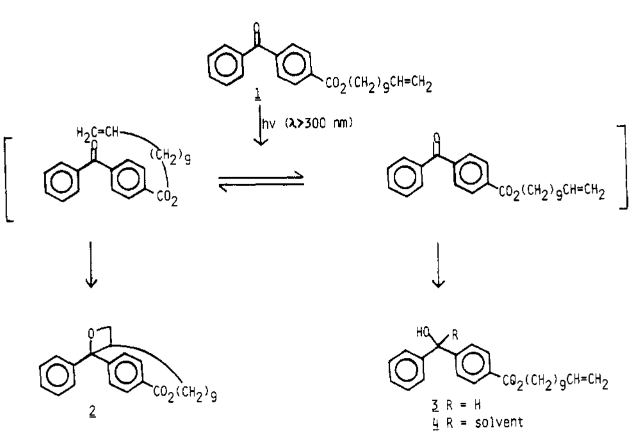

Table I
Photoreduction Product Ratios [3]/([4′] + [4″]) from 1.1 × 10^{-3} M 1 in N_2-Saturated *n*-Hexane

% convrsn[a] of 1 (±5%)	[3]/([4′] + [4″]) (±0.2)	% convrsn[a] of 1 (±5%)	[3]/([4′] + [4″]) (±0.2)
46	3.9	80	4.0
53	4.1	87	4.2
66	4.0	92	5.1
73	4.1	98	3.6
			4.1[b]

[a] Percent conversion based on disappearance of 1 as monitored by HPLC. [b] Average value.

efficiency for photodimerization of the solute upon stretching the LDPE films was reported.[7a]

In this paper, we investigate the photochemistry of a conformationally labile dopant, ω-undecylenyl benzophenone-4-carboxylate (1),[8] in stretched and unstretched LDPE and in *n*-hexane (a model isotropic solvent). We find that the polyethylene matrix imposes unexpected restrictions upon the conformations of 1 and that the photochemistry is altered by stretching the LDPE films.

Results and Discussion. Upon irradiation (λ > 300 nm) in hydrocarbon media, 1 can cyclize to yield oxetane 2 or be photoreduced to 3 and/or 4 via H abstraction from solvent[9] (Scheme I). These processes are believed to occur from the $^3(n,\pi^*)$ state of the ketone.[8-10] While intermolecular photoreduction can occur from many conformations of 1 in LDPE, formation of the intramolecular oxetane demands a specific orientation between the carbonyl and olefinic groups (which can be achieved only through chain coiling). If this orientation is not present upon initial excitation, it must be achieved within the triplet lifetime of 1 if 2 is to be formed.[10] A useful probe of the ability of 1 to attain the appropriate geometry is given by the competition between formation of 2 and the photoreduction products 3 and 4.

The product ratio ([3] + [4])/[2] is experimentally very difficult to measure in LDPE (vide infra). However, it was determined at several percent conversions in *n*-hexane (Table I). The ratios of carbinol 3 to the sum of the two observed hexane-incorporated reduction products (4′ and 4″; R = hexyl in Scheme I) were independent of percent conversion and demonstrate that a constant fraction of ketyl radicals from 4 yields 3 and 4′ + 4″: ([3] + [4′] + [4″])/[2] can be expressed as [3](1 + *a*)/[2], where *a* = ([4′] + [4″])/[3]. Thus, the ratio [3]/[2] is a valid competitive measure of the reactivity channels of triplets of 1 in *n*-hexane.

That this relationship holds even in LDPE was demonstrated by measuring ([3] + [4])/[2] at 95% conversion of 1 in stretched (s) and unstretched (u) films (Table II).

Table II
Product Ratios from Irradiation of 1 in LDPE[a] and in *n*-Hexane

solvent	% convrsn	[3]/[2] unstretched	[3]/[2] stretched	$\gamma = ([3]/[2])_u/([3]/[2])_s$
n-hexane	95	24 (30)[b]	24 (30)[b]	
LDPE	95	6.1	2.9	2.1
		4.2 (8.4)[b]	1.5 (3.5)[b]	2.9 (2.1)[c]
	70	8.6	3.7	2.3
		7.5	2.9	2.6
	30	8.4	3.0	2.8
		6.2	2.6	2.4

[a] Each data point represents an average of 6–8 experiments wherein segments of the film were cleaned, doped, stretched, and irradiated under identical conditions from a given sheet. Sheet-to-sheet differences are reflected in the individual [3]/[2] ratios within a column. [b] ([3 + 4])/[2] for LDPE and ([3] + [4′] + [4″])/[2] for *n*-hexane. [c] $[([3] + [4])/[2]]_u/[([3] + [4])/[2]]_s$.

As they must be if the partitioning of ketyl radicals remains constant, the two ratios $\gamma = ([3]/[2])_u/([3]/[2])_s$ and $(([3] + [4])/[2])_u/(([3] + [4])/[2])_s$ are equal within experimental error. This experiment and the observation that γ does not vary with percent conversion indicate indirectly that the fractionation of each radical intermediate between reversion to 1 and formation of a specific product is affected only slightly by stretching LDPE. Therefore, γ in Table II is a comprehensive reflection of the course of the reactions of triplet 1. In essence, it measures the influence of LDPE stretching on the conformationally dependent channels leading to intramolecular cyclization and intermolecular reduction.

Each entry row in Table II is for data obtained with the same batch of 1-doped LDPE. It was found that even though one type of LDPE was employed, reproducible results were limited to films which shared the same history. Each doped film was cut into several pieces, half of which were stretched manually to 4.5 times their original length. When compared internally (along a row of Table II), the results are self-consistent. The value of γ remains ca. 2.5 regardless of the percent conversion or sample employed. This observation, in essence, requires that the relative probability of intramolecular oxetane formation be greater in stretched than in unstretched LDPE. It also indicates that all molecules of 1 experience similar sites of solvation within LDPE. The data show that the intramolecular reaction mode is even less favored in the low-viscosity isotropic solvent *n*-hexane. These results can be analyzed further only upon examination of the probable solubilization sites for 1 in LDPE.

There is ample experimental evidence that LDPE contains a distribution of crystalline regions (wherein chains are tightly and regularly packed) and amorphous or defect regions (wherein chains are somewhat random).[11] A wide variety of spectroscopic techniques (ESR,[12] ^{2}H NMR,[13] and linear dichroism[14]) have been employed to investigate the environments of molecules doped into the defect sites. These studies show that mechanical stretching of LDPE orders the random chains macroscopically and microscopically and allows the dopants to experience a more ordered environment.[11-14] However, almost all of the dopants studied thus far are conformationally inflexible molecules whose sensitivity to changes in the arrangement of solvent molecules is limited to electronic interactions. An exception is the work of Li and Guillet.[7b]

The many degrees of rotational freedom available to 1 make it extremely sensitive to changes in its local environment. Its shape can respond to (microscopic) alterations in the solvent cavity, should they be incurred during (macroscopic) stretching. In fact, the data demonstrate that *stretching of LDPE increases coiling of 1*! We had anticipated the opposite result: a priori, it seemed reasonable that stretching LDPE would favor extended conformers of 1 incapable of forming 2 and from which intermolecular hydrogen abstraction can arise.

To the best of our knowledge, this observation is without precedent. It begs further experimentation and suggests that the shapes of defect sites are altered upon film stretching, but in ways which have not been anticipated.[11-14] Our basis for future work assumes that stretching decreases the *volume* of defect sites (making coiling of 1 tighter) without grossly influencing their shape. Future studies to test this hypothesis will be conducted.

Experimental Section. ^{1}H NMR spectra were obtained with a 90-MHz Fourier transform Bruker Model HFX-100 spectrometer. Analytical high-pressure liquid chromatographic analyses were performed on a Waters Model 6000A HPLC (UV detection: 254 nm) connected to a Varian (Model CDS 111) integrator. A Waters Rad-Pak B silica column was used with 99/1 (v/v) chloroform/ethyl acetate as eluent.

Materials. ω-Undecylenyl benzophenone-4-carboxylate (**1**) and its corresponding intramolecular oxetane **2** were synthesized by the method of Bichan and Winnik[8] and gave the same spectral characteristics as those reported.[8] Carbinol **3** was synthesized by irradiation ($\lambda > 300$ nm) of **1** (1.1×10^{-3} M) in isopropyl alcohol or *n*-hexane[8] and purified by TLC (silica gel/chloroform). For **3**: mp 88–90 °C; UV (methanol) 240 nm; IR (KBr) 3500, 3080, 2960, 1760, 1620, 1603, 1290 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.2–2.2 (19 H, m), 3.15 (1 H, s, hydroxyl proton), 4.3 (2 H, t, J = 6 Hz), 4.89 (1 H, br s), 5.03 (1 H, br d, J = 6 Hz), 5.5–6.1 (1 H, m), 7.0–7.7 (7 H, m), 7.83 (2 H, d, J = 8 Hz).

Irradiation of **1** in *n*-hexane gave, in addition to **3**, two other products, **4′** and **4″**. On the basis of the UV absorption and IR spectra of their mixture, **4′** and **4″** are hexane-incorporated reduction products. UV (methanol) 240 nm; IR (neat) 3500, 3080, 2960, 1760, 1620, 1603, 1290 cm^{-1}.

Low-density polyethylene films (LDPE) were "Sclairfilm" 300 LT-1 supplied by Du Pont Canada, Inc. Before stretching, the films were 76.2 μm thick and of density 0.92 g/cm^3. Samples of stretched and unstretched LDPE doped with **1** were prepared as follows. A strip of film (6 cm × 1 cm) was soaked in chloroform for 12 h at 25 °C to remove antioxidants. The film was then dried in a stream of nitrogen and immersed in a 10^{-3} M chloroform solution of **1** for 12 h at 25 °C. The film surface was thoroughly rinsed with methanol and dried with a stream of nitrogen. UV and IR spectra were recorded to confirm that **1** had been doped into the film. The concentration of **1** was ~0.9 M in the unstretched film based upon the spectral measurements. The doped film was stretched by hand to approximately 4.5 times its initial length, the surface of the film was washed thoroughly with methanol (to remove any "salted out" **1**) and was dried under a stream of nitrogen.

Irradiation and Analyses. The unstretched and stretched films were irradiated for 1.5–2.5 h at room temperature with a Hanovia 450-W medium-pressure mercury lamp fitted with a Pyrex filter. The UV absorption maximum at 254 nm shifted to 240 nm during irradiation. Percent conversions were determined by monitoring the loss of UV absorption at 254 nm in the films. After irradiation, the films were soaked in chloroform to remove products. Extraction was carried out repeatedly until the chloroform was barren.

Even after the chloroform extractions, some absorption at 240 nm persisted, indicating cross-linking of **1** to LDPE. The percent cross-linking of sample with 95% conversion was estimated from the difference in absorption before and after the extraction procedure by assuming that **2**, **3**, and **4** had the same molar extinction coefficient at 240 nm. The extracts were combined, concentrated, and analyzed by HPLC to obtain the product ratios.

Diffusion of **1**–**3** from LDPE. In order to check for diffusional loss of solutes from LDPE films,[7b,15] **1**, **2**, and **3** were individually doped into three separate strips. Each was allowed to stand at room temperature for ca. 3 h while UV spectra were recorded at intervals of ca. 15 min. After each spectrum was recorded, the film was washed with methanol to remove any material that might have diffused to the surface. No decrease in the optical density at 254 nm was observed for **1**, **2**, or **3** in the stretched and unstretched films. Similarly, it was found that **1** could be removed quantitatively from LDPE films.

Determination of [**3**]/([**4′**] + [**4″**]) in *n*-Hexane. A nitrogen-saturated (1.1×10^{-3} M) solution of **1** in *n*-hexane was irradiated as before. Aliquots were withdrawn at regular intervals and analyzed by HPLC. The peak corresponding to **3** was known uniquely from the irradiation of **1** in isopropyl alcohol.

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On Novel Crystalline Forms of Poly(γ-benzyl L-glutamate)

Previous papers[1-3] have indicated that poly(γ-benzyl L-glutamate) (PBLG) films composed of α-helices exhibit two crystal modifications, denoted forms B and C, when they are cast from solutions in various solvents. Form B, prepared from dimethylformamide, benzyl alcohol, and benzyl propionate, exhibits a well-defined X-ray pattern offering a three-dimensional monoclinic unit cell. In contrast, form C, cast from halogenated hydrocarbons such as chloroform, shows an X-ray pattern with some reflections on the equatorial line and continuous scatterings on other layer lines. Form C is, thus, described by a structure with a poor periodicity in the lateral packing as well as a displacement of mutual levels of α-helices along the axes. The basic structure cannot be altered by heat treatment around 180 °C, showing that these two forms differ from each other not in the side-chain conformation but in the way of disposition of two up and down directed chains.[3] In crystalline form B there is an alternating disposition of two chains while form C is considered to have a random displacement of the chains.[3,4]

Here, we report the structural characteristics of two highly crystalline forms, so-called forms D and E, which are newly prepared from the former kind of solvent. Forms D and E are characterized by extraordinarily large hexagonal unit cells with 7 chains and 19 chains included, respectively, and by having an ordered structure of side chains with restriction of their rotational motion.

PBLG (M_w = 80 000) was synthesized by the conventional NCA method using triethylamine as an initiator. Films of forms D and E were prepared by slow casting solutions in benzyl propionate over 2 weeks at 65 and 80 °C, respectively, where the nonvolatile solvents were evaporated under vacuum. Casting rate as well as temperature is a significant factor in making these forms. Quick casting produces only form B and somewhat prolonged casting over 2–3 days facilitates the coexistence of form B with form D or E, suggesting that both forms have been gradually altered from form B in the casting process. Wide-angle X-ray patterns were recorded with flat-plate and cylindrical cameras, using a Rigaku-Denki X-ray generator with Ni-filtered Cu Kα radiation. Dielectric measurements were conducted with a mutual inductance bridge (TR-1C), a detector (BAD-18), and an oscillator (WBG-3B) manufactured by Ando Electric Co., Ltd., over a frequency range from 30 Hz to 1 MHz.

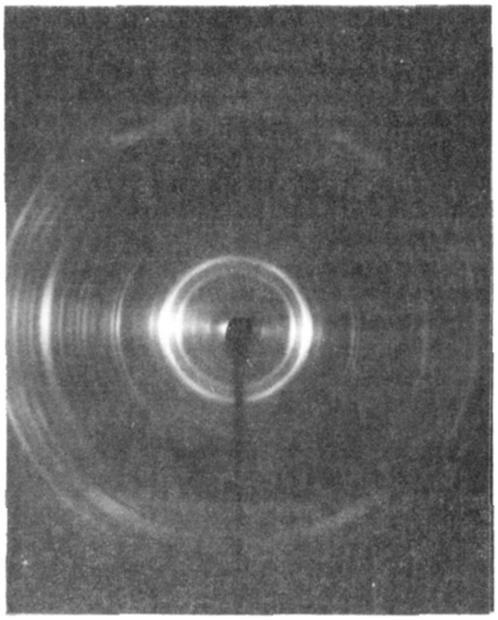

Figure 1. X-ray diffraction pattern of form E film. The X-ray beam was irradiated parallel to the film surface. The film surface is in the vertical direction.

Table I
X-ray Data of PBLG Form E

index[a]	d_{obsd}, Å	d_{calcd},[a] Å	intensity[b]
100		55.74	
110	32.4	32.18	w
200	28.0	27.87	w
210	21.0	21.07	w
300	18.5	18.58	vw
220	16.2	16.09	vvw
310	15.5	15.46	s
400	14.1	13.93	vw
320	12.8	12.79	vs
410	12.1	12.16	m
500	11.2	11.15	vvw
330	10.7	10.73	w
420		10.53	
510	10.1	10.01	vvw
600		9.29	
430		9.16	
520	8.92	8.93	vw
610	8.53	8.50	vvw
440		8.05	
530 700		7.96	
620	7.72	7.73	s
710	7.38	7.38	m

[a] Calculated spacings and indices are based on a hexagonal lattice with an edge of 64.3_6 Å. [b] Code: vs = very strong, s = strong, m = moderate, w = weak, vw = very weak, and vvw = very very weak.

Figure 1 shows the X-ray diffraction pattern of form E film where the X-ray beam was aimed parallel to the film surface. From the numerous reflections, one can easily see that this form is a highly crystalline form, which so far has not been observed in this kind of synthetic polypeptide. The spacings of reflections on the equatorial line, ranging from 40 to 7 Å, are well elucidated and are listed in Table I. For the reflections on other layer lines, however, no estimation of spacings was possible because of overlapping of the reflections due to poor orientation. The intense "turn" layer line, associated with the pitch length of the α-helix,[5] appears at 5.25 Å from the equator, as can be seen from Figure 1. We further find another layer line at 10.5 Å. The tilted pattern represents the 1.5-Å meridional reflection. A set of layer lines, hence, are equally spaced about 1/10.5 Å^{-1} apart, indicating that the helical conformation is not of the 18-residue, 5-turn type but of the 7-residue, 2-turn type.[6,7] Turning to the equatorial pattern, it is surprising that the spacing of the first reflection is 32.4 Å, which is remarkably larger than the diameter (=15 Å) of the molecule. This demands an extraordinarily large unit cell in the lateral packing structure. In fact, 16

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